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⑤⑥ **Method for manufacturing lithographic printing plates.**

⑤⑦ A method for manufacturing lithographic printing plate which comprises imagewise exposing a presensitized plate for use in making lithographic printing plates and supplying a developer onto the surface of the exposed presensitized plate to develop the presensitized plate, the method characterized in that a developer having a viscosity measured at 25 ° C ranging from 5 to 10,000 cps is employed. The method is improved so that a constant amount of fresh developer is constantly supplied to be able to perform stable development processing and it can suitably be applied to "disposable development system".

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## Method for Manufacturing Lithographic Printing Plates

### BACKGROUND OF THE INVENTION

The present invention relates to a method for manufacturing lithographic printing plates comprising developing a presensitized plate for use in making the same and more specifically to a method for manufacturing lithographic printing plates which is improved so that a constant amount of fresh developer is constantly supplied to be able to perform stable development processing and which can suitably be applied to "disposable development system".

When a large amount of presensitized plate for use in making lithographic printing plates (hereinafter referred to as "PS plate(s)") are developed, an automatic developing machine is in general used.

Such an automatic developing machine comprises a device for horizontally conveying a PS plate, a bath for containing a developer and a spray device. In such a developing machine, a method comprising spraying the developer pumped up onto the PS plate, which has been exposed to light, through a spray nozzle to develop the same while horizontally conveying the exposed PS plates is generally adopted. Alternatively, it is also known to develop such a PS plate by immersing and conveying the plate in the developer by means of, for instance, dipped guide rolls.

In such a processing in which an automatic developing machine is used, the developer is repeatedly used from the viewpoint of economy. As a result, various problems arise, for instance, the concentrations of components of the light-sensitive layer dissolved in the developer gradually increase, correspondingly the developing ability of the developer is deteriorated and feculence and sludge are formed in the developer. Moreover, if the developer is an alkali solution, it absorbs carbon dioxide in the air to cause deterioration.

In addition to the foregoing deterioration of the developer, the automatic developing machine is contaminated with spatter of sprayed developer. Therefore, it is required to frequently exchange the developer and wash the automatic developing machine.

When a large number of PS plates are processed in accordance with a method in which a circulated developer is used in order to eliminate these disadvantages, there has been proposed a method for supplementing a replenisher therefor as disclosed in Japanese Patent Un-examined Publication (hereunder referred to as "J.P. KOKAI") Nos. 55-115039 and 58-95349. This method makes it possible to perform stable processing for a long period of time. However, this method also has problems such that complicated handlings such as fine adjustments and set up are required.

As a means for eliminating drawbacks accompanied by the method for processing PS plates utilizing an automatic developing machine while circulating a large amount of developer to reuse the same, J.P. KOKAI Nos. 48-29505 and 55-32044 and U.S. Patent No. 4,222,656 disclose a method which comprises supplying a constant amount of a fresh developer onto the exposed surface of a PS plate which has been exposed to light to develop the plate and then removing the developer from the plate to dispose the used developer (this method is hereinafter referred to as "disposable developing system").

In this disposable developing system, it should be necessary to uniformly hold, on a PS plate, the smallest required amount of a developer for a constant time period. However, the developer is likely to be non-uniformly distributed thereon practically and hence uneven development is often caused. This is particularly true at the edge portion and in the cases where the substrate of the PS plate has uneven portions. To solve this problem, various steps such as supplementation of a large amount of a developer and use of a brush or a sponge to uniformly distribute the developer have been taken. However, these steps require the use of the developer in an amount greater than the smallest required amount thereof and this is not preferred in view of running cost.

More severe problem of the disposable developing system is that double side type PS plates having light-sensitive layers on both sides cannot be processed simultaneously. In other word, if the double side type PS plates are developed by the disposable developing system, it is necessary to uniformly hold the required amount of a developer even on the back side of the plate, which is conveyed horizontally, for constant time period, but the developer cannot be maintained thereon but it is dropped or concentrated at the lower portions. Thus, the uniform development of the whole surface is impossible. For this reason, both sides are separately processed one by one when such a double side type PS plate is developed by the disposable developing system. However, uneven development is often observed because the developer passes around behind the back surface.

In order to eliminate the aforementioned drawbacks, it has been thought that the double side type PS plate is vertically conveyed while supplying a developer to both sides thereof. The developer runs down

from the surface of the plate, but is not held thereon uniformly which leads to uneven development.

## SUMMARY OF THE INVENTION

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An object of the present invention is to provide a method for development processing PS plates which makes it possible to solve the problem associated with the disposable developing system, which is stable for along time and which is economically favorable.

Another object of the present invention is to provide a method for manufacturing lithographic printing  
10 plates which can stably process both sides of double side type PS plates simultaneously.

A further object of the present invention is to provide a method for manufacturing lithographic printing plates which can always provide uniform finishing although the smallest amount of a developer is used.

The aforementioned objects of the invention associated with the disposable developing system can be achieved by adjusting the viscosity of a developer to a proper range. Accordingly, the present invention  
15 relates to a method for manufacturing lithographic printing plate comprising imagewise exposing a presensitized plate for use in making lithographic printing plates and supplying a developer onto the surface of the exposed presensitized plate to develop the presensitized plate and the method is characterized by using a developer having a viscosity measured at 25 ° C ranging from 5 to 10,000 cps.

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## DETAILED EXPLANATION OF THE INVENTION

The present invention will hereinafter be explained in more detail.

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### I. Developer

The developer used in the present invention will be detailed below.

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#### (i) Viscosity

Viscosity of the developer used in the invention preferably ranges from 5 to 10,000 cps, more preferably 50 to 5,000 cps. This is because if the viscosity is less than the lower limit, it is not possible to  
35 uniformly distribute the developer on the surface of the PS plate, while if it exceeds the upper limit, the circulation of developer and the supplementation thereof on the surface of the plate are hindered.

#### (ii) Thickener

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The developer for PS plates used in the invention usually comprises a surfactant, an organic solvent, an alkaline agent and inorganic salts. The developer used herein further comprises a thickener for adjusting the viscosity thereof.

Any thickener may be used in the developer so far as they can adjust the viscosity within a desired  
45 range, 5 to 10,000 cps. Preferred are those which can increase the viscosity of the developer by adding it only in a small amount and which exert no influence on the developing ability of the developer. As such thickeners, there may be used a variety of water-soluble polymeric compounds or fine powder of silicates. Among these, preferred are natural or synthetic water-soluble polymers.

Examples of natural polymers are such starches as sweet potato starch, potato starch, tapioca starch,  
50 wheat starch and corn starch; such polymers obtained from seaweeds as carrageenan, laminaran, seaweed mannan, funorin, Irish moss, agar and sodium alginate; such plant mucin as tororo-aoi mucin, mannan, quince seed gum, pectin, tragacanth gum, karaya gum, guar bean gum, locust bean gum, arabic gum, carob gum and benzoin gum; such microorganism mucins as homopolysaccharides (e.g., dextran, glucan and levan) and heteropolysaccharides (e.g., succinoglucan and xanthan gum; and such proteins as glue,  
55 gelatin, casein and collagen..

Examples of seminatural (semisynthetic) water-soluble polymers include, in addition to propylene glycol alginate, such fibrin derivatives as viscose, methyl cellulose, ethyl cellulose, methyl ethyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, hydroxypropyl cellulose, hydroxypropyl methyl cellulose,

hydroxypropyl ethyl cellulose and hydroxypropyl methyl cellulose and processed starches. Examples of the processed starches include such roasted starches as white dextrin, yellow dextrin and British gum; such enzyme modified dextrins as enzyme dextrin and Shardingner enzyme dextrin; such acid decomposed starches as soluble starch; such oxidized starches as dialdehyde starch, such alpha starches as modified  
 5 alpha starch and non-modified alpha starch; such esterified starches as phosphate starch, fatty acid starch, sulfate starch, nitrate starch, xanthogenic acid starch and carbamic acid starch; such etherified starches as carboxyalkyl starch, hydroxyalkyl starch, sulfoalkyl starch, cyanoethyl starch, allyl starch, benzyl starch, carbamyl starch and dialkylamino starch; such cross-linked starches as methylol cross-linked starch, hydroxyalkyl cross-linked starch, phosphoric acid cross-linked starch and dicarboxylic acid cross-linked  
 10 starch; and such starch grafted copolymers as starch polyacrylamide copolymer, starch polyacrylic acid copolymer, starch polyvinyl acetate copolymer, starch polyacrylonitrile copolymer, cationic starch polyacrylate polymer, cationic starch vinyl polymer copolymer, starch polystyrene maleic acid copolymer and starch polyethylene oxide copolymer.

Examples of the synthetic water-soluble polymers are polyvinyl alcohol, such modified polyvinyl  
 15 alcohols and polyvinyl alcohol partially modified with acetal, allyl modified polyvinyl alcohol, polyvinyl methyl ether, polyvinyl ethyl ether and polyvinyl isobutyl ether; such polyacrylic acid derivatives and polymethacrylic acid derivatives as sodium polyacrylate, partially saponified polyacrylate, partially saponified polyacrylate copolymer, polymethacrylic acid salts and polyacrylamide; polyethylene glycol, polyvinylpyrrolidone, copolymer of polyvinyl pyrrolidone and vinyl acetate, carboxyvinyl polymer, styrene-maleic  
 20 anhydride copolymer, styrene-crotonic acid copolymer, polystyrene sulfonic acid salts and polymer of 2-acrylamido-2-methylpropane sulfonic acid, copolymer thereof with other monomers or salts thereof. Among these, semisynthetic and synthetic polymers are preferred because they can impart the long term stability of the developer. These water-soluble polymeric compounds may be used along or in combination. These water-soluble polymeric compounds are preferably used in an amount required for achieving a desired  
 25 viscosity of the developer and the practical amount thereof varies depending on the molecular weight of the polymeric compounds used and the solubility thereof in water. Therefore, the amount of the water-soluble polymers cannot be defined uniquely, but it preferably ranges from 0.5 to 20% by weight based on the total weight of the developer.

### 30 (iii) Composition of the Developer

The composition of the developer may vary depending on the kinds of the PS plates to be processed. Typical examples thereof for developing, for instance, a negative working PS plate mainly composed of p-diazodiphenylamine include those composed of benzyl alcohol, an anionic surfactant and a water-soluble  
 35 sulfite as disclosed in Japanese Patent Publication for Opposition Purpose (hereinafter referred to as "J.P. KOKOKU") No. 56-42860. The developer used in the invention further comprises aforesaid thickener in addition to the foregoing components.

When o-quinonediazide type PS plates are processed, the composition of the developer is not  
 40 restricted to a specific one so far as it is alkaline, but it is preferred to adjust pH to not less than about 10.5 at 25 °C taking into consideration factors such as processing time and complete dissolution or removal of exposed portions.

#### 45 a) Alkaline Agent

Examples of useful alkaline agents are such an alkaline inorganic agents as sodium silicate, potassium silicate, ammonium silicate, sodium hydroxide, lithium hydroxide, potassium hydroxide, trisodium phosphate, disodium hydrogen phosphate, tripotassium phosphate, dipotassium hydrogen phosphate, triam-  
 50 monium phosphate, diammonium hydrogen phosphate, sodium metasilicate, sodium bicarbonate, sodium carbonate, potassium carbonate or ammonium carbonate; such an organic alkaline agent as mono-, di- or tri-ethanolamine or ammonium tetraalkyl hydroxide; and ammonium organosilicate.

Most preferred are silicates among others. The amount thereof used generally ranges from about 0.5 to about 10% by weight, preferably 1 to 8% by weight and more preferably 1 to 6% by weight on the basis of  
 55 the total weight of the developer.

The silicates represented by the formula:  $\text{SiO}_2 \cdot \text{MO}_2$  (wherein M is an alkali metal). As the molar ratio:  $\text{SiO}_2/\text{MO}_2$  becomes small, the development processing proceeds more rapidly. In particular in the method for manufacturing lithographic printing plates of the invention wherein operations for promoting development

such as rubbing with a brush or a sponge are not performed or only a simple development promoting operation is carried out, the molar ratio is preferably not more than 1.2. In addition, if a water-soluble polymeric compound is used as a thickener, it sometimes consumes alkali. In such a case, it is preferred to supplement alkaline agents.

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#### b) Surfactant

Moreover, the developer the PS plates having o-quinonediazide type light-sensitive layer may contain  
10 surfactants such as anionic or amphoteric surfactants as sodium alkylnaphthalene sulfonate and N-tetradecyl-N,N-dihydroxyethyl betaine as disclosed in J.P. KOKAI No. 50-51324 and such nonionic surfactants as tetramethyldecyne diol as disclosed in U.S. Patent No. 4,374,920, in order to protect the image portions and to thus prevent excess development.

It is also preferable to add a surfactant to such kind of developer for enhancing wettability of the PS  
15 plate. Examples of such surfactants are a part of anionic surfactants such as sodium alkyl diphenyl ether disulfonates and sodium alkyl sulfonates, but particularly preferred are fluorine type surfactants having perfluoroalkyl groups in the molecule.

As such fluorine type surfactants, there may be mentioned such an anionic type one as perfluoroalkyl-carboxylic acid salts, perfluoroalkylsulfonic acid salts or perfluoroalkyl phosphoric acid salts; such an  
20 amphoteric type one as perfluoroalkyl betaine; such a cationic one as perfluoroalkyl trimethylammonium salts; and such a nonionic type one as perfluoroalkylamine oxides, perfluoroalkyl ethylene oxide adducts, oligomers containing perfluoroalkyl groups and hydrophilic groups, oligomers having perfluoroalkyl groups and oleophilic groups, oligomers having perfluoroalkyl, hydrophilic and oleophilic groups or urethanes having perfluoroalkyl groups and oleophilic groups. These surfactants are desirably used in an amount  
25 required for reducing the surface tension of the developer to a desired level, but the amount thereof preferably 0.001 to 3% by weight and more preferably 0.003 to 0.5% by weight on the basis of the total weight of the developer.

The developer used in the present invention may further contain various other surfactants such as those described in U.S. Patent No. 4, 374,920 and J.P. KOKAI No. 50-51324 already cited above in addition to the  
30 foregoing surfactants.

#### c) Other Additives

The developer used in the invention may comprise the following additives for the purpose of enhancing the developing quality. Examples of such additives include neutral salts such as NaCl, KCl and KBr as disclosed in J.P. KOKAI No. 58-75152; chelating agents such as EDTA and NTA as disclosed in J.P. KOKAI No. 58-190952; complexes such as  $(\text{Co}(\text{NH}_3)_6)\text{Cl}_3$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  as disclosed in J.P. KOKAI No. 59-121336; cationic polymers such as methyl chloride quaternary product of p-dimethylaminomethyl polystyrene as disclosed in J.P. KOKAI No. 55-95946; amphoteric polyelectrolytes such as copolymer of vinylbenzyl trimethyl ammonium chloride and sodium acrylate as disclosed in J.P. KOKAI No. 56-142528; reducing inorganic salts such as sodium sulfite as disclosed in J.P. KOKAI No. 57-192952; inorganic lithium compounds such as lithium chloride as disclosed in J.P. KOKAI No. 58-59444; organolithium compounds such as lithium benzoate as disclosed in J.P. KOKAI No. 50-34442; organometallic surfactants containing  
40 Si and Ti as disclosed in J.P. KOKAI No. 59-75255; organoboron compounds as disclosed in J.P. KOKAI No. 59-84241; quaternary ammonium salts such as tetraalkyl ammonium oxide as disclosed in European Patent No. 101,010; and organic solvents such as benzyl alcohols and ethylene glycol monophenyl ether.

#### 50 II. PS Plates

The PS plates processed by the method of this invention are not restricted to specific ones and typical examples thereof include those composed of an aluminum plate provided thereon with a light-sensitive layer consisting of a mixture of a diazo resin (a salt of condensed product of p-diazodiphenylamine and  
55 paraformaldehyde) and shellac as disclosed in U.K. Patent No. 1,350,521; negative working PS plates composed of an aluminum plate provided thereon with a light-sensitive layer consisting of a mixture of a diazo resin and a polymer which comprises hydroxyethyl methacrylate units and hydroxyethyl acrylate units as main repeating units as disclosed in U.K. Patent Nos. 1,460,978 and 1,505,739; positive working PS

plates composed of an aluminum plate provided thereon with a light-sensitive layer consisting of o-quinonediazide compound; and negative working PS plates comprising a light-sensitive layer consisting essentially of o-quinonediazide compound as disclosed in J.P. KOKOKU No. 56-14970, which show the negative working effect after imagewise exposing, heating, exposing the whole surface thereof to light and development processing. Besides, negative working PS plates having a photopolymerizable light-sensitive layer or a photocross-likable light-sensitive layer can likewise be treated by the method of the present invention.

The method for manufacturing lithographic printing plates according to the present invention will be detailed below referring to a PS plate composed of a substrate provided thereon with a light-sensitive layer which comprises an o-quinonediazide compound, particularly an o-naphthoquinonediazide compound as an example.

#### (i) Substrate

Examples of preferred substrates are metal plates such as aluminum (inclusive of aluminum alloys), zinc, tin, copper and iron plates and composite plates thereof; plastic films or sheets such as cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, cellulose nitrate, polyethylene terephthalate, polyethylene, polypropylene, polystyrene, polycarbonate and polyvinyl acetal films or sheets; paper or a plastic film on which the foregoing metal is deposited or with which a film of the foregoing metal is laminated; and composite sheets such as that obtained by bonding a polyethylene terephthalate film and an aluminum sheet. Particularly preferred are those having aluminum surface because of their high dimensional stability.

The surface of these substrates is in general subjected to surface processing for the purposes of making it hydrophilic, preventing, from causing, a harmful reaction with the light-sensitive layer subsequently provided thereon and enhancing the adhesion between the substrate and the light-sensitive layer. For instance, a substrate having an aluminum surface is preferably grained mechanically, chemically or electrically and then dipped in an aqueous solution of, for instance, sodium silicate, potassium fluorozirconate or a phosphate, or subjected to anodization treatment. In this respect, the anodization treatment can be performed by electrolyzing by passing an electric current through an aluminum plate serving as an anode in an electrolyte comprised of an aqueous solution containing one or more of inorganic salts of inorganic acids such as sulfuric acid, chromic acid, phosphoric acid and boric acid; organic acids such as oxalic acid and sulfamic acid and salts thereof. The use of silicate electrodeposition as disclosed in U.S. Patent No. 3,658,662 is also effective in the invention.

Specific examples of such substrates are an aluminum plate which is grained and then is dipped in a solution of sodium silicate as disclosed in U.S. Patent No. 2,714,066; an aluminum plate which is anodized and then is dipped in a solution of an alkali metal silicate as disclosed in J.P. KOKOKU No. 47-5125; and a substrate which is electrolytically grained and is then anodized as disclosed in J.P. KOKOKU No. 46-27481 and J.P. KOKAI Nos. 52-58602 and 52-30503.

#### (ii) Light-sensitive Layer

The light-sensitive layer which is provided on the substrate is preferably obtained from, particularly o-naphthoquinonediazide compounds as already mentioned above and examples thereof are described in a variety of publications such as U.S. Patent Nos. 3,041,110; 3,046,111; 3,046,112; 3,046,115; 3,046,118; 3,046,119; 3,046,120; 3,046,121; 3,046,122; 3,046,123; 3,061,430; 3,162,809; 3,106,465; 3,635,709; and 3,647,443. All these can effectively be used in the invention. Particularly preferred are o-naphthoquinonediazido-sulfonic acid esters or o-naphthoquinonediazido-carboxylic acid esters of aromatic hydroxyl compounds and o-naphthoquinonediazido-sulfonic acid amides or o-naphthoquinonediazido-carboxylic acid amides of aromatic amine compounds. In particular, a condensed product of pyrogallol and acetone which is esterified with o-naphthoquinonediazido-sulfonic acid as disclosed in U.S. Patent No. 3,635,709; a polyester having a hydroxyl group at the terminal which is esterified with o-naphthoquinonediazido-sulfonic acid or o-naphthoquinonediazido-carboxylic acid as disclosed in U.S. Patent No. 4,028,111; a homopolymer of p-hydroxystyrene or a copolymer thereof with another copolymerizable monomer which is esterified with o-naphthoquinonediazido-sulfonic acid or o-naphthoquinonediazido-carboxylic acid as disclosed in U.K. Patent No. 1,494,043.

These o-naphthoquinonediazide compounds may be used alone, but it is preferred to use it in

combination with an alkali-soluble resin. Examples thereof include novolak type phenol resins, more specifically phenol-formaldehyde resin, o-cresol/formaldehyde resin and m-cresol/formaldehyde resin. It is more preferable to simultaneously use a condensate of a phenol or cresol substituted with alkyl groups having 3 to 8 carbon atoms and formaldehyde such as 1-butyl-phenol/formaldehyde resin, in addition to the foregoing phenol resin, as disclosed in J.P. KOKAI No. 50-125806. The amount of these alkali-soluble resins used ranges from about 50 to about 85% by weight, preferably 60 to 80% by weight on the basis of the total weight of the light-sensitive layer.

The light-sensitive layer further comprises dyes, plasticizers, components for imparting print-out properties to the layer according to need. As such additives, any conventionally known ones can be used. Preferred examples of dyes are those soluble in alcohols such as C.I. 26, 105 (Oil Red RR), C.I. 21, 260 (Oil Scarlet #308), C.I. 74, 350 (Oil Blue), C.I. 52, 015 (Methylene Blue), C.I. 42, 555 (Crystal Violet), which serve to impart sufficient contrast between image areas and non-image areas of a PS plate after exposure and development. These dyes are used in an amount of not more than about 7% by weight of the total weight of the light-sensitive composition.

Examples of effective plasticizers include such phthalates as dimethyl phthalate, diethyl phthalate, dibutyl phthalate, diisobutyl phthalate, dioctyl phthalate, octyl capryl phthalate, dicyclohexyl phthalate, ditridecyl phthalate, butyl benzyl phthalate, diisodecyl phthalate and diaryl phthalate; such glycol esters as dimethyl glycol phthalate, ethylphthalyl ethyl glycolate, methylphthalyl ethyl glycolate, butylphthalyl butyl glycolate and triethylene glycol dicaprylate; such phosphoric acid esters as tricresyl phosphate and triphenyl phosphate; such aliphatic dibasic acid esters as diisobutyl adipate, dioctyl adipate, dimethyl sebacate, dibutyl sebacate, dioctyl azelate and dibutyl maleate; polyglycidyl methacrylate, triethyl citrate, glycerin triacetyl ester and butyl laurate. These plasticizers is in general used in an amount of not more than about 5% by weight of the total weight of the light-sensitive composition.

The components having print out properties are agents or compositions for obtaining a visible image immediately after imagewise exposure of the light-sensitive layer of a PS plate. Examples thereof are a pH indicator such as those described in U.K. Patent No. 1,041,463; a combination of o-naphthoquinonediazido-4-sulfonyl chloride and a dye as disclosed in U.S. Patent No. 3,969,118; and photochromic compounds as disclosed in J.P. KOKOKU No. 44-6413. Alternatively, it is also possible to improve sensitivity of the light-sensitive layer by adding massive acid anhydride to the layer as disclosed in J.P. KOKAI No. 52-80022.

A desired light-sensitive layer can be obtained by applying a solution of the foregoing light-sensitive composition in a proper solvent onto the surface of a substrate. As solvents preferably used there may be mentioned such glycol ethers as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, methoxyethyl acetate; such ketones as acetone, methyl ethyl ketone and cyclohexanone; and such chlorinated hydrocarbons as ethylene dichloride. The coated amount of the light-sensitive composition generally ranges from about 0.5 to about 7 g/m<sup>2</sup>, and preferably 1.0 to 3 g/m<sup>2</sup>.

### III. Development Processing

The positive working PS plate is exposed, through a transparency, to light from a light source rich in actinic rays such as a carbon arc lamp, a mercury lamp, a metal halide lamp, a xenon lamp or a tungsten lamp. The exposed areas thereof is made alkaline-soluble by such exposure and, therefore, the exposed areas can be dissolved out with a developer, i.e., an alkali solution.

In the method of this invention, the supply of the developer onto the exposed PS plate can be performed by injecting, spraying or dropwise adding the developer to the surface of the plate utilizing a shower pipe or a nozzle; or by coating the surface of the plate with the developer supplied from a developer supply member which is disposed so as to or so as not to come into contact with the surface thereof.

In order to supply the developer to a PS plate with a developer supply member which comes into contact with the surface of the plate, a method comprising rubbing the surface of the plate with a member having water absorption properties such as a sponge or cloth; a method comprising synchronizing the speed of conveyed PS plate and that of a roller made from a non-water absorbing member such as rubber or a member having water absorption properties such as aforesaid sponge or cloth; or a method comprising dispensing the developer with a wire bar can be employed.

On the other hand, when the developer is supplied to the PS plate by a developer supply member which is disposed so as not to come into contact with the surface of the plate, a method comprising passing the PS plate through a fine gap in which the developer is stored; a method comprising coming the surface of the plate into contact with the developer which is supplied in the form of a drop suspended from the developer supply member due to surface tension; or a method comprising passing through a slit formed on

the side of a cylindrical container for developer can be adopted. Alternatively, a method comprising flowing out the developer from a fine slit formed on the upper face of a cylindrical container for developer while horizontally conveying the PS plate over the upper face thereof to supply the developer is very favorable for treating the back surface of double side type PS plates. When such a double side type PS plate is developed, two sides may be developed by the same or different developer supply members. Likewise, both sides may be developed with the same or different developers. The method of the present invention can preferably be adopted even when a positive working PS plate and a negative working PS plate are processed with the same developer.

Moreover, the method of this invention is favorably adopted when the PS plates are vertically arranged and conveyed upward or downward or toward right or left since the developer can be easily maintained on the surfaces thereof.

The amount of the developer supplied by such methods ranges from 30 to 500 ml and preferably 50 to 200 ml per 1 m<sup>2</sup> of the processed PS plate.

In the method of the invention, the disposable developing system is preferably adopted. Therefore, it is desirable that the developer supplied to the surface of the PS plate be scraped off to dispose the same after maintaining it on the surface of the plate for a constant time period.

The PS plates thus developed are subsequently subjected to conventional processes such as water washing, retouching and gumming processes to complete lithographic printing plates, as in the conventional processing of the PS plates.

The method of this invention makes it possible to uniformly hold a small amount of a developer on both faces of a PS plate, in the disposable developing system and, therefore, it becomes possible to perform the development processing in which even the back face of the PS plate is uniformly developed. In addition, the method of the invention also makes it possible to perform uniform development using only a small amount of a developer, or ultimately an amount just required for development. Moreover, once the developer is uniformly supplied to the surface of the PS plate, the method of the present invention makes it possible to uniformly maintain the developer on the plate without using a complicated device or with using a simple device and, therefore, maintenance of the device is very easy and the development processing can be stably carried out without any troubles even when the automatic developing machine is operated over a long time.

The present invention will hereunder be described with reference to the following Examples in more detail, but the present invention is not restricted to the following specific Examples at all. Moreover, the effects practically achieved by the invention will also be discussed in comparison with Comparative Examples.

#### Examples 1 to 6 and Comparative Example 1

A grained 2S aluminum plate was immersed, for one minute, in a solution of sodium hydroxide having a concentration of 2% by weight maintained at 40 °C to carry out etching of the aluminum plate. After washing the etched plate, the plate was immersed in a sulfuric acid/chromic acid mixture for one minute to expose the pure aluminum surface thereof. Then the plate was immersed in 20% by weight of sulfuric acid maintained at 30 °C to carry out anodization at a DC voltage of 1.5 V and a current density of 2 A/dm<sup>2</sup> for two minutes followed by washing with water and drying. PS plates were prepared by applying a solution of a light-sensitive composition having the following composition onto the aluminum plate thus treated in an amount of 2 g/m<sup>2</sup> (weighed after drying) and then drying.



Component	Amount (g)
Naphthoquinone-1,2-diazido(2)-5-sulfonate of acetone/pyrogallol resin (synthesized by a method disclosed in Example 1 of U.S. Patent No. 3,635,709)	5
t-Butylphenol/formaldehyde resin (PS-50530; available from Sumitomo Jurays Co., Ltd.)	0.5
Cresol/formaldehyde resin (Hitanol #3110; available from Hitachi Chemical Co., Ltd.)	5
Methyl ethyl ketone	50
Cyclohexanone	40

The PS plate thus obtained was exposed, for 30 seconds, to light from a 3 KW metal halide lamp (PLANO PS LIGHT provided with a light source: Toshiba Metal Halide Lamp MU 2000-2-OL type; available from Fuji Photo Film Co., Ltd.) in a distance of 1m within a vacuum printing frame.

Then, developers A to G listed in Table I were prepared and the viscosity thereof was determined by using a B-type viscometer.

Then, an automatic developing machine of horizontally conveying type, equipped with a wire bar as a dispensing means, disclosed in J.P. KOKAI No. 62-59957, was provided. Each developer A to G was applied to the surface of the exposed PS plate whose light-sensitive layer was disposed upward in an amount of about 200 ml per 1 m<sup>2</sup> of the plate. After 40 seconds, the developer of the PS plate was squeezed out with a pair of squeeze rolls. The plate was then washed in a subsequent water washing bath and the plate was examined whether there was uneven development or not. The results observed are summarized in Table I. The developer A could not uniformly held on the surface of the plate and the portions at which the thickness of the developer was thin could not completely developed.

When the developer G was used, it could be uniformly held on the plate, but some contaminated developer was rarely adhered to the squeeze rolls, which was sometimes transferred to the plates subsequently treated.

When the developers B to F were used, good results were obtained in every cases.

Table I

Ex. No.	C.E.1	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Developer	A	B	C	D	E	F	G
Component of developer (g)							
Methyl cellulose *)	0	14	25	50	75	90	100
1K Potassium silicate	55	55	55	55	55	55	55
48 wt% aq. soln. of potassium hydroxide	25	25	25	25	25	25	25
Water	950	950	950	950	950	950	950
Viscosity (cps)	2.8	8	20	150	1,050	4,000	9,000
Uneven development	+	-	-	-	-	-	-

\*) Available from Shin-Etsu Chemical Co., Ltd. under the trade name of METOLOSE 65SH50.

Estimation criteria of "Development":

+ : even

- : uneven

#### Examples 7 to 12

A double side type PS plate was prepared by treating both sides of an aluminum plate and applying light-sensitive layers as in Examples 1 to 6, both sides of the PS plate was imagewise exposed to light as in Examples 1 to 6.

Then a horizontally conveying type automatic developing machine of disposable developing system as

disclosed in Example 1 of J.P. KOKAI No. 62-59958 and 81 of a rinse solution having the following formulation which had been diluted 8 times was charged into the second bath thereof.

Formulation of the Rinse Solution	
85 wt% Aqueous solution of phosphoric acid	48 g
Sodium hydroxide	19.2 g
Sodium dioctylsulfosuccinate	24 g
Sodium dodecyl diphenyl ether disulfonate	24 g
Silicone antifoaming agent TSA-731	0.08 g
Water	875 g

The double side type PS plate was developed with the developers A to G prepared above in the automatic developing machine. The results obtained are summarized in Table II. The developability of the upper face thereof with respect to these developer was completely the same as those observed in Examples 1 to 6.

When the developer A is applied to the back face of the plate, the developer was dropped from the plate and many parts thereof could not be developed. When the developer B was used, satisfactory development was observed although part of the developer was dropped.

While the developers C to G were uniformly held on the back face of the plate and they provided quite satisfactory results. In this respect, when the developer G was used, there was observed the contaminants were transferred to the squeeze rolls as in Example 6.

Table II

Ex. No.	C.E.2	Ex. 7	Ex. 8	Ex. 9	Ex.10	Ex.11	Ex.12
Developer	A	B	C	D	E	F	G
Viscosity (cps)	2.8	8	20	150	1,050	4,000	9,000
Development of upper face	+	-	-	-	-	-	-
Uniformity of developer on back face	x	zy	zy	z	z	z	z
The estimation criteria of uneven development is the same as those described above in connection with Table I.							
Those of "Uniformity of developer on back face" are as follows:							
x : bad							
y : permissible							
z : good							

## Claims

1. A method for manufacturing lithographic printing plate comprising imagewise exposing a presensitized plate for use in making lithographic printing plates and supplying a developer onto the surface of the exposed presensitized plate to develop the presensitized plate, the method characterized in that a developer having a viscosity measured at 25° C ranging from 5 to 10,000 cps is employed.
2. A method of claim 1 wherein the system for development is a disposable development system.
3. A method of claim 1 wherein the viscosity of the developer ranges from 50 to 5,000 cps.
4. A method of claim 1 wherein the viscosity of the developer is adjusted by the addition of at least one thickener.
5. A method of claim 4 wherein the developer comprises surfactants, organic solvents, alkali agents, inorganic salts and thickeners.
6. A method of claim 4 wherein the thickener is at least one water-soluble polymeric compound or fine powder of silicate.
7. A method of claim 6 wherein the thickener is at least one natural or synthetic water-soluble polymer.

8. A method of claim 7 wherein the thickener is at least one natural polymer and is selected from the group consisting of sweet potato starch, potato starch, tapioca starch, wheat starch and corn starch; carrageenan, laminaran, seaweed mannan, funorin, Irish moss, agar and sodium alginate; tororo-aoi mucin, mannan, quince seed gum, pectin, tragacanth gum, karaya gum, guar bean gum, locust bean gum, arabic gum, carob gum and benzoin gum; dextran, glucan and levan; succinoglucan and xanthan gum; glue, gelatin, casein and collagen.

9. A method of claim 7 wherein the thickener is at least one seminatural water-soluble polymer and is selected from the group consisting of propylene glycol alginate, viscose, methyl cellulose, ethyl cellulose, methyl ethyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, hydroxypropyl cellulose, hydroxypropyl methyl cellulose, hydroxypropyl ethyl-cellulose and hydroxypropyl methyl cellulose and processed starches.

10. A method of claim 9 wherein the processed starch is selected from white dextrin, yellow dextrin and British gum; enzyme dextrin and Sharding enzyme dextrin; soluble starch; dialdehyde starch; modified alpha starch and non-modified alpha starch; phosphate starch, fatty acid starch, sulfate starch, nitrate starch, xanthogenic acid starch and carbamic acid starch; carboxyalkyl starch, hydroxyalkyl starch, sulfoalkyl starch, cyanoethyl starch, allyl starch, benzyl starch, carbamyl starch and dialkylamino starch; methylol cross-linked starch, hydroxyalkyl cross-linked starch, phosphoric acid cross-linked starch and dicarboxylic acid cross-linked starch; starch polyacrylamide copolymer, starch polyacrylic acid copolymer, starch polyvinyl acetate copolymer, starch polyacrylonitrile copolymer, cationic starch polyacrylate copolymer, cationic starch vinyl polymer copolymer, starch polystyrene maleic acid copolymer and starch polyethylene oxide copolymer.

11. A method of claim 7 wherein the thickener is at least one synthetic water-soluble polymer and is selected from polyvinyl alcohol, polyvinyl alcohol partially modified with acetal, allyl modified polyvinyl alcohol, polyvinyl methyl ether, polyvinyl ethyl ether and polyvinyl isobutyl ether; sodium polyacrylate, partially saponified polyacrylate, partially saponified polyacrylate copolymer, polymethacrylic acid salts and polyacrylamide; polyethylene glycol, polyvinylpyrrolidone, copolymer of polyvinyl pyrrolidone and vinyl acetate, carboxyvinyl polymer, styrene-maleic anhydride copolymer, styrene-crotonic acid copolymer, polystyrene sulfonic acid salts and polymer of 2-acrylamido-2-methylpropane sulfonic acid, copolymer thereof with other monomers or salts thereof.

12. A method of claim 7 wherein the thickener is semisynthetic and/or synthetic polymer.

13. A method of claim 4 wherein the amount of the thickener ranges from 0.5 to 20% by weight on the basis of the total weight of the developer.

14. A method of claim 1 wherein pH of the developer at 25 °C is not less than about 10.5.

15. A method of claim 1 wherein the developer comprises silicates and the amount thereof ranges from 1 to 8% by weight on the basis of the total weight of the developer.

16. A method of claim 1 wherein the silicate is represented by the formula:  $\text{SiO}_2 \cdot \text{MO}_2$  (wherein M is an alkali metal) and the molar ratio:  $\text{SiO}_2/\text{MO}_2$  is not more than 1.2.

17. A method of claim 1 wherein the surfactant is selected from fluorine type ones having perfluoroalkyl groups in the molecule.

18. A method of claim 17 wherein the fluorine type surfactant having perfluoroalkyl groups in the molecule is selected from the group consisting of perfluoroalkylcarboxylic acid salts, perfluoroalkylsulfonic acid salts or perfluoroalkyl phosphoric acid salts; perfluoroalkyl betaine; perfluoroalkyl trimethylammonium salts; perfluoroalkylamine oxides, perfluoroalkyl ethylene oxide adducts, oligomers containing perfluoroalkyl groups and hydrophilic groups, oligomers having perfluoroalkyl groups and oleophilic groups, oligomers having perfluoroalkyl, hydrophilic and oleophilic groups or urethanes having perfluoroalkyl groups and oleophilic groups.

19. A method of claim 1 wherein the amount of the surfactant ranges from 0.001 to 3% by weight on the basis of the total weight of the developer.

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54 **Method for manufacturing lithographic printing plates.**

57 A method for manufacturing lithographic printing plate which comprises imagewise exposing a presensitized plate for use in making lithographic printing plates and supplying a developer onto the surface of the exposed presensitized plate to develop the presensitized plate, the method characterized in that a developer having a viscosity measured at 25 ° C ranging from 5 to 10,000 cps is employed. The method is improved so that a constant amount of fresh developer is constantly supplied to be able to perform stable development processing and it can suitably be applied to "disposable development system".

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	US-A-2 318 322 (C.E. MEULENDYKE) * Page 2, column 1, line 15 - page 2, column 1, line 20; claim 1 * ---	1-18	G 03 F 7/26
X	US-A-3 608 464 (R.E. HARRELL et al.) * Column 2, line 54 * ---	1	
X	GB-A-1 102 952 (W.H. HOWSON LI.,) * The whole document * ---	1-18	
X	RESEARCH DISCLOSURE, vol. 177, no. 116, December 1973, pages 101-103, no. 11664, Havant, GB; "Novel composition for the stripping of photosensitive surfaces usable in the preparation of photographic resists" * The whole article * ---	1-18	
X	EP-A-0 178 495 (ALLIED CORP.) * The whole document * ---	18	
X	EP-A-0 129 106 (ALLIED CORP.) * The whole document * ---	18	TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
A	FR-A-2 172 914 (VISUAL GRAPHICS CORP.) * The whole document * -----	1-18	G 03 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 07-11-1989	Examiner RASSCHAERT A.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			